

Safety Alert

Violent Failures of Older Compressed Gas Cylinders

Two recent explosions at UC Santa Barbara and the US Army lab at Edgewood, Maryland involved the violent failure of cylinders containing liquefied compressed gases. These incidents are vivid reminders that workers need to be aware of compressed gas cylinder shelf life limits.

In July, 2005 a cylinder of anhydrous hydrogen fluoride (HF) failed explosively in an unoccupied UC Santa Barbara lab (see photos 1 and 2), causing considerable damage. It now appears that moisture entered the cylinder and promoted corrosion. The fluorine in the HF reacted with the iron in the cylinder wall, promoted by moisture, to form iron (ferric) fluoride. HF in a cylinder is mainly a liquid with a very low vapor pressure, between only 5 to 15-pounds per square inch, gauge (psig). The corrosion process formed hydrogen, a true gas, and the pressure inside the cylinder increased as more and more hydrogen was formed by corrosion. In addition, the chemical reaction with the metal in the cylinder weakened the cylinder until the cylinder failed. The customary shelf life for HF cylinders is one or two years, depending on the vendor. The cylinder that exploded was at least seven years old.



Figure 1 The remains of the HF cylinder.



Figure 2. Laboratory equipment damaged by the exploding HF cylinder.

In April, 2005, a cylinder containing a residual amount of hydrogen cyanide (HCN) burst in a US Army lab at Edgewood, Maryland. HCN in a cylinder is also a liquid with the gas in the space above it. Like HF, the vapor pressure of HCN is very low, essentially 0 psig at room temperature and about 10 psig at 100°F. With the presence of heat, over time the HCN forms a polymer with itself. A tap on the cylinder could cause a flake of polymer from above the pool of liquid to fall onto the film of polymer. This will cause the remaining pooled liquid to polymerize extremely rapidly, producing hot gas that will cause the cylinder to fail explosively. Older cylinders can be extremely shock sensitive so they need to be removed by specially trained hazardous materials crews. The Army's laboratory activities at Edgewood were disrupted for months while other cylinders of HCN were removed. For this reason the customary storage lifetime for cylinders of hydrogen cyanide is just six months.

Concerns

- The ChemTrack inventory indicates that there are no HF or HCN cylinders at this time. However cylinders of either gas could create significant hazards if they are brought onsite in the future.
- Vendors set shelf life limits for compressed gases to avoid hazards, and to protect the quality of the gas. It is important to ascertain when manufacturer shelf life limits are based on safety (rather than product quality concerns) and adhere to safety-based shelf life limits.
- Moisture needs to be kept out of cylinders containing anhydrous HF. Moisture also needs to be kept out of HCN cylinders because it promotes polymerization.

Note: Moisture needs to be kept out of cylinders that contain hydrogen chloride or hydrogen bromide as well, to avoid leaks from corroded valve components (not overpressurization).

Recommended Actions for LLNL Employees

1. Ensure that all vendor-filled cylinders have a ChemTrack label, including lecture (sample) bottles. Cylinders filled or refilled onsite with custom gas mixtures should also be ChemTrack labeled or properly identified to avoid costly disposal issues.
2. Return HF and HCN cylinders nearing the ends of their shelf lives to the vendor. If any cylinders of HF or HCN are found that are questionable, immediately contact your ES&H Team.
3. If the cylinder is more than two years old, contact your ES&H Team for assistance in determining pressure build-up. The pressure could be hundreds or a few thousand psig due to hydrogen evolution. The pressure of a cylinder of pure liquid HF that has not produced hydrogen will be between about 5-15 psig under normal conditions.
4. Keep moisture out of HF cylinders to minimize hydrogen buildup. This can be done by placing a suitable moisture trap between the gas outlet or apparatus the cylinder is connected to and the cylinder.

Note: Also keep moisture out of hydrogen chloride and hydrogen bromide cylinders to avoid leaks caused by corrosion.

5. If you order HCN, or if HCN is an ingredient in gas mixtures, check with the manufacturer for the cylinder's shelf life. The shelf life for cylinders of pure HCN will typically be just six months.
6. Share any information you find concerning safety-based shelf life limits for chemicals, including gases in cylinders, with the Chemical & Biological Safety Program at ext. 2-5215. The information will be sent to ChemTrack where it will be posted on the "LLNL Limited Shelf Life" list. This list is available by clicking the ChemTrack "Reports" button, clicking on the "ES&H" button, and scrolling down to "LLNL Limited Shelf Life."
7. Check the "LLNL Limited Shelf Life" list to see if you have chemicals listed there. Work with your ES&H Team to have them evaluated for hazards and to be disposed of properly.

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